RE: USSN 10/798,584

I, the undersigned, who have prepared English translation which is attached herewith, hereby declare that the aforementioned translation is true and correct translation of officially certified copy of the Korean Patent Application No. 10-1999-0067746 filed on December 31, 1999.

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Date: November 10, 2006

KOREAN INTELLECTUAL PROPERTY OFFICE

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Date of Application:	December 31, 1999
Application Number:	Patent Application No. 10-1999-0067746
Applicant(s)	LG CHEMICAL CO. LTD.

COMMISSIONER

APPLICATION FOR PATENT

To the Commissioner of
the Korean Intellectual Property Office

FILING DATE: December 31, 1999

TITLE: ELECTRONIC DEVICE COMPRISING ORGANIC COMPOUND HAVING P-TYPE SEMICONDUCTING CHARACTERISTICS

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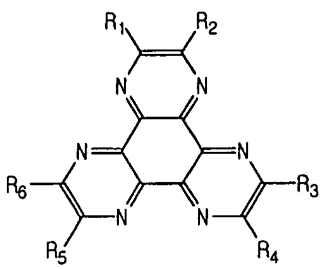
Submitted herewith is an application identified above pursuant to Article 42 of the Patent Act.

【ABSTRACT】

【SUMMARY】

The present invention relates to an electronic device comprising organic compounds having p-type semiconductor characteristics, and operation voltage of the device can be lowered and the life of the device can be prolonged by providing an electronic device comprising a hexaazatriphenylene-based organic compound represented by the following Chemical Formula 1 as a hole-injecting and/or hole-transporting material which may form interface with anode:

[Chemical Formula 1]



(wherein, R_1 to R_6 are independently or simultaneously selected from the group consisting of hydrogen atom, C_1-C_{12} hydrocarbon, halogen, alkoxy, arylamine, ester, amide, imide, aromatic hydrocarbon, heterocyclic compound, nitro, and nitrile (-CN) group).

【REPRESENTATIVE FIGURE】

Figure 1

【INDEX】

organic light emitting device, operating voltage, hole, brightness, p-type semiconductor

【 SPECIFICATION】

【 TITLE OF THE INVENTION】

Light emitting device comprising organic compounds having p-type semiconductor characteristics

【 BRIEF DESCRIPTION OF THE FIGURES】

FIG. 1 is a simplified cross-sectional view of an organic light-emitting diode according to an example of the present invention.

FIG. 2 is a simplified cross-sectional view of an organic light-emitting diode having different structure according to the another example of the present invention.

FIG. 3 is a graph showing the correlation between brightness and the voltage of the organic light-emitting device of the present invention.

FIG. 4 is a graph showing the decrease of relative brightness of the organic light-emitting device of the present invention according to operating time.

* Reference numerals *

(11) and (21) indicates a transparent substrate,

(12) and (22) an anode,

(13) a hole-injecting layer,

(14) a hole-transporting layer,

(15) and (25) a light-emitting layer,

(16) and (26) an electron-transporting layer,

(17) and (27) a cathode layer, and

(24) a hole-injecting and transporting layer.

【 DETAILED DESCRIPTION】

【 OBJECT OF THE INVENTION】

【 FIELD OF THE INVENTION AND DESCRIPTION OF THE RELATED ART】

[Field of the Invention]

The present invention relates to an electronic device comprising organic compounds having p-type semiconductor characteristics, and particularly to a an electronic device which can be operated by low voltage and has prolonged life by using a hexaazatriphenylene based organic

compound as a hole-injecting and/or hole-transporting material which may form interface with anode.

[Description of the Related Art]

Basically, organic light emitting devices comprise anode, cathode, and an organic materials forming a light emitting layer between the two electrodes. Hitherto, it is impossible to produce a device having high efficiency because holes or electrons injection from the electrode to the light emitting layer is difficult. To make a device having high efficiency, the organic material existing between the electrodes must be easy to receive electrons or holes and the introduced carriers must be able to move rapidly from the organic layer to light emitting layer. Furthermore, the emission of photons by recombination of the carriers must be far from the electrodes to prevent quenching of exiton by the metal electrodes.

The above problems may be solved by introducing a two layered device that consists of hole-transporting material and electron-transporting material between a cathode and an anode, as disclosed in U.S. Pat. No. 4,359,507. The hole-transporting material used therein is a triphenyl amine-based compound that rapidly receives holes from ITO, which is an anode, and transports the holes to 8-hydroxyquinoline aluminum complex (Alq3), which is an electron-transporting and light emitting material, simultaneously. Therefore, the operating voltage and the efficiency of the device are largely enhanced, and when the thickness of the device decreased to about 100 nm, the device may operate by voltage of 10 V or less.

The operating voltage of the light-emitting devices was more lowered by inserting a hole-injecting material between the triphenyl amine-based compounds, and thus it was possible to make a more stable device. As the examples the material, , U.S. Pat. No. 4,356,429 discloses metal phthalocyanine and U.S. Pat. No. 5,540,999 discloses polythiophene based polymer, U.S. Pat. No. 5,616,427 discloses quinacridone type materials, and the materials forms a stable interface with ITO or lowers the hole injection barrier between hole-transporting materials. For the similar purpose, the life of the organic light-emitting device was increased by introducing a layer of poly[3,4-(ethylene-1,2-dioxy)thiophene (PEDOT), which is a conducting polymer, on the ITO electrode in polymer light-emitting device. The introduction of the hole-injecting material helps to prevent device short of the organic light-emitting device in which the thickness of organic material between electrodes is merely 100-200 nm.

However, when the thick hole-injecting layer is formed, the layer may absorb light

emitted from the organic light-emitting device or change the spectrum of the light by introducing the hole-injection material, because the hole-injecting materials generally have a small band gap and absorb visible light. Furthermore, if the hole-injecting material is not a conducting material, the operating voltage of the device rises in proportion to the thickness of the hole-injecting layer

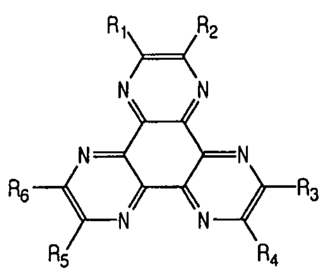
【 TECHNICAL SUBJECTS OF THE INVENTION】

In order to achieve the above objects, the present invention provides an organic light-emitting device which can be operated by low voltage and has prolonged life by using a hexaazatriphenylene based organic compound as a hole-injecting and/or hole-transporting material which may form interface with anode.

【 DETAILED DESCRIPTION AND THE PREFERRED EMBODIMENTS】

In order to achieve these objects, the present invention provides an organic light-emitting device comprising a hexaazatriphenylene (hereinafter 'HAT') based organic compound represented by the following Chemical Formual 1 in at least one layer of hole-injecting layer and hole-transporting layer:

[Chemical Formula 1]



(wherein, R_1 to R_6 are independently or simultaneously selected from the group consisting of hydrogen atom, C_1-C_{12} hydrocarbon, halogen, alkoxy, arylamine, ester, amide, imide, aromatic hydrocarbon, heterocyclic compound, nitro, and nitrile (-CN) group).

That is, the present invention provides an organic light emitting device comprising a transparent substrate, anode, hole-injecting layer comprising the organic compound represented by Chemical Formula 1, light emitting and electron transporting layer, and cathode, in order.

Furthermore, the device of the present invention may further comprise a hole-transporting layer between the anode and the hole-injecting layer, and the hole-transporting layer may comprise the compound represented by Chemical Formula 1 or may not.

Hereinafter, the present invention will now be explained in more detail.

First, the compound represented by the Chemical Formula 1 used in the electronic device

of the present invention will be explained.

It is disclosed in U.S. Pat. No. 4,780,536 that the compound of the Chemical Formula 1 can be used as a cross-linking agent of heat resistance polymers, and it has been predicted that the compound can be used as an n-type organic semiconductor that transports electrons in electronic device based on organic substance owing to its low reduction potential (Polymer Preprint *40*, 404, 1999). Particularly, it is known that the compound of the Chemical Formula 1, when each R is nitrile group, has a reduction potential of only -0.01 V and thus it clearly has n-type organic semiconductor characteristics.

The present invention may decrease the operation voltage of electronic devices and improve the life of devices by employing the organic compound of the Chemical Formula 1 as a hole-injecting and hole-transporting material which requires low reduction potential on the contrary to the prediction of the prior art. It is estimated that the low operation voltage and improved life of the electronic devices is due to that the compound represented by Chemical Formula 1 forms chemical interface, which is stronger than physical interface, with the surface of ITO when the compound has strong polar substituents. That is, the hexaazatriphenylene part of the organic compound represented by Chemical Formula 1 having conjugation bond enables to transport the holes and the strong polar substituents of the compound enables some chemical bond with the surface of ITO having hydroxy group.

Hereinafter, the organic light emitting device comprising the compound represented by Chemical Formula 2 will now be explained in detail.

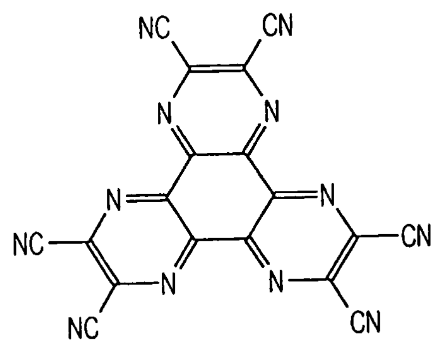
The present invention provides a multi stacked thin film typed organic light-emitting device to identify a role of the organic compound represented by Chemical Formula 1 as a hole-injecting and hole-transporting material. The organic light-emitting device comprises a transparent substrate, anode, hole-injecting layer comprising the organic compound represented by Chemical Formula 1, light emitting and electron transporting layer, and cathode in order, or comprises a transparent substrate, anode, hole-injecting layer comprising the organic compound represented by Chemical Formula 1, hole-transporting layer, light emitting and electron transporting layer, and cathode in order.

Furthermore, it is possible to give light emitting property to the hole-transporting layer by slightly doping fluorescent dyes to the hole-transporting layer or light-emitting layer, as well as to divide the light-emitting and electron transporting layer into the light-emitting layer and the

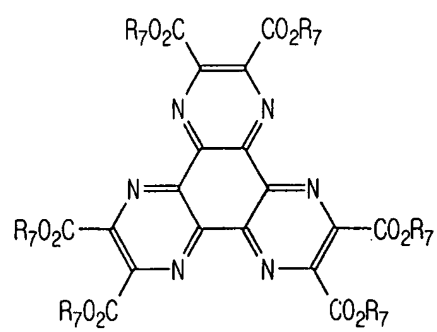
electron-transporting layer for enhancing the efficiency of the organic light-emitting device.

When the compound represented by Chemical Formula 1 of the present invention has a role of hole-injecting layer by forming a thin film on the ITO, the interface of the layer and the ITO is more stable as the substituents represented by R_1 to R_6 have more strong polarity and are capable of strong interaction with hydroxyl group on the surface of ITO. The preferable organic compound represented by Chemical Formula 1 satisfying the above requirements may be the compounds represented by Chemical Formulae 2 to 6.

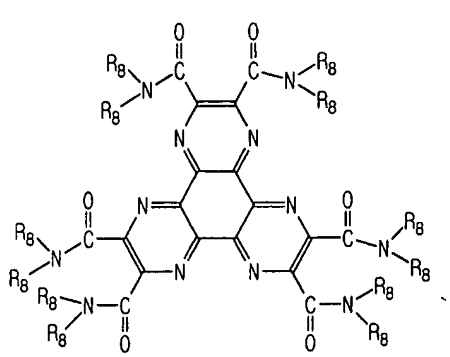
[Chemical Formula 2]



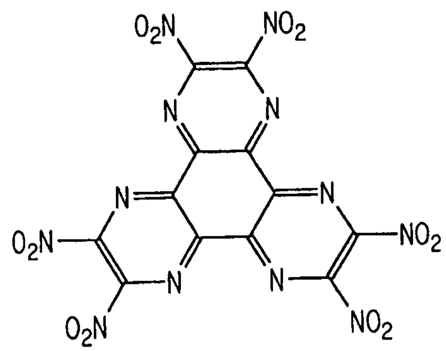
[Chemical Formula 3]



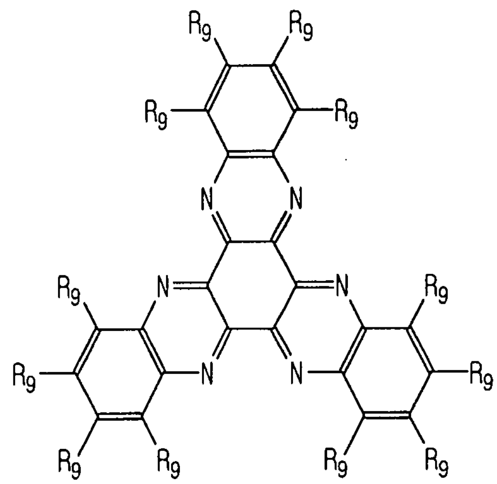
[Chemical Formula 4]



[Chemical Formula 5]



[Chemical Formula 6]



(in Chemical Formulae 3 and 4, the substituent of R_7 and R_8 are independently or simultaneously a hydrogen, a C_1-C_{30} hydrocarbon, or a aromatic group,

in Chemical Formula 6, the substituent of R_9 is independently or simultaneously hydrogen, C_1-C_{30} hydrocarbon, aromatic group, nitrile ester, amide, alkoxy, or amine).

The compound represented by Chemical Forumla 1 that is used as a hole-injecting and transporting material constitutes at least one layer of the multi-layered structure of thin films in the organic light-emitting device, and especially, a hole-injecting layer receiving holes from ITO, a layer transporting holes to a hole-injecting and light-emitting layer, or a layer only transporting holes.

Hereinafter, the organic light-emitting device of the present invention will be explained by referring FIGs. 1 and 2 in more detail.

The general structure of organic light-emitting device consists of multi-layers as shown in FIG. 1, in which e.g., an indium tin oxide thin film is coated on a transparent substrate (11) to

form a transparent electrode, i.e., an anode (12), on which a hole-injecting layer (13), a hole-transporting layer (14), a light-emitting layer (15), an electron-transporting layer (16) and a cathode layer (17) are sequentially laminated. Alternatively, as shown in FIG. 2, it may have a structure consisting of a transparent substrate (21), a transparent electrode (22) a layer simultaneously performing hole-injecting and transporting layer (14), a light-emitting layer (25), an electron-transporting layer (26) and a cathode layer (27).

When the compound of Chemical Formula 1 of the present invention is used as a hole-injecting and transporting material of the organic light-emitting device, the device may have more or less number of multi-layers between the anode and the cathode, and may have a plurality of light-emitting layer in addition to the structure of FIGs. 1 and 2 as necessary. Furthermore, the compound of Chemical Formula 1 of the present invention may be similarly applied to various devices requiring superior hole-transporting ability in addition to the organic light-emitting device.

As the transparent substrate (11, 21), glass, plastic, metal, wafer, etc. can be used, and more preferably, glass or plastics of amorphous properties can be preferably used, and substrates having appropriate mechanical strength and surface flatness such as metal or wafer can be used according to the use.

In addition, as a transparent electrode (12, 22), metal oxides or oxides of mixed metals such as indium tin oxide, zinc oxide, indium zinc oxide, etc. can be used, and conductive polymers in which appropriate dopants are added to polymers such as PEDOT, polyaniline, polypyrrole, polythiophene, etc., can be used, and metals having high work function such as gold can be used as necessary.

The compound represented by the Chemical Formula 1 can be used as a material forming the hole-injecting layer (13) in FIG. 1, and the compound may be used in combination with other kinds of compound satisfying Chemical Formula 1 as a material forming the hole-transporting layer (14) . When the organic compound of the Chemical Formula 1 is not used as a hole-transporting layer (14), the hole-transporting layer can be formed with conventional arylamine type compounds or polycyclic aromatic compounds. As examples of the hole-transporting material, 4,4'-bis[N-(1-naphthyl)-N-phenyl-amino]biphenyl (NPB) can be mentioned.

The organic compound of the Chemical Formula 1 can be used as a hole-injecting and transporting material in the organic light-emitting device shown in FIG. 2. When the compound

of Chemical Formula 1 is used to a hole-injecting and transporting layer (14), the thick of the layer may be from 0.1 to 10,000 nm, and more preferably from 0.5 to 1,000 nm.

The light-emitting layer (15, 25) is a layer, in which electrons and holes injected from two opposite electrodes are recombined and emit light. Generally, the light-emitting layer employs materials having high fluorescence efficiency and which is hard to crystallize. The light emitted from the light-emitting layer relates to band gap of the material composing the light-emitting layer. As representative examples, the compounds having blue band gap and composing the light-emitting layer are disclosed in U.S. Pat. Nos. 5,645,948, 5,840,217, 5,150,006, and 5,366,811, and especially, 8-hydroxyquinoline aluminum salt (Alq3) is used as a compound having a green band gap. In addition to the light-emitting materials, any compound having fluorescence characteristics and capable of receiving holes from a hole-transporting layer and receiving electrons from a electron-transporting layer may be used as a compound composing the light-emitting layer. Recently, a compound having high fluorescence efficiency is slightly doped to the compound consisting the light-emitting layer to enhance the light-emitting efficiency and the life of the device.

The electron-transporting layer (16, 26) in FIGS. 1 and 2, which receives electrons from a cathode (17, 27) and transports them to a light-emitting layer, employs material that smoothly injects electrons from a cathode and simultaneously forms a stable interface with the cathode. The representative example of the material is Alq3, which emits green light.

As material forming a cathode (17, 27), material having low work function is used so as to easily inject electrons into an electron-transporting layer(16, 26). As examples of the materials, alloys such as lithium-aluminum alloy, magnesium-silver alloy, etc. can be used, and LiF, Li_2O, etc. may be used by forming as a thin film (0.1-1 nm) laminated between an aluminum electrode and electon-injecting material so as to enhance the injection of electrons. Furthermore, the stable interface between electrode and electron-transporting layer can be fortified by mix-depositing the electron-transporting material and electrode material. In addition to the cathode material, any compound that can form a stable interface between electrode and electron-transporting layer and easily inject electrons into an electron-transporting layer may be used as a cathode material.

The organic light-emitting devices shown in FIGs. 1 and 2 are illustrate as a means to use an ability of the compound represented by Chemical Formula 1 such as a thermal stability, a

capability of receiving and transporting holes and of forming an interface with metal oxides.

The compound of the Chemical Formula 1 can be applied to an organic thin film transistor requiring a property similar to that of the compound of the Chemical Formula 1, a photovoltaic cell, an OPC drum (organic photo conductor drum) laser printer or a cloying press, etc. Particularly, the compound of the Chemical Formula 1 is suitable for a p-type organic thin film transistor, since the organic thin film transistor must form a stable interface with a fate insulator and rapidly transport holes from a source to a drain. As shown above, the compound of the Chemical Formula 1, especially the compound of the Chemical Formula 2, was predicted that may have characteristics of n-type organic semiconductor (Polymer Preprint 40, 404, 1999), however it is revealed in the present invention that the compound acts as a p-type semiconductor having superior hole-transporting ability as shown the following Examples. The compound of Chemical Formula 1 is applicable to OPC drum by using the superior hole-transporting ability, and specifically, may be used to fabricate a high speed copy machine and a printer requiring a compound having rapid hole-transporting speed.

[EXAMPLES]

The present invention is described in detail through the following EXAMPLES and COMPARATIVE EXAMPLES. However, these EXAMPLES are for illustrating the present invention and not for limiting the present invention.

(Example 1)

A glass substrate coated with a thin film of ITO (indium tin oxide) was ultrasonically cleaned in an solution comprising a cleaning agent, dried, and transferred into a plasma cleaning device. The substrate was cleaned with oxygen plasma by 50 W of power for 5 minutes while introducing 100 mtorr of oxygen therein, and transferred to a vacuum vapor deposition device. A hole-injecting layer having thickness of 750 _ was formed by thermal vacuum depositing the compound of Chemical Formula 2 satisfying Chemical Formula 1 over the prepared ITO transparent electrode. NPB (400 _) as a hole-transporting material and Alq3 (600 _) having both of electron-transporting and light-emitting properties were deposited on the hole-injecting layer. Then, an electrode was formed by depositing 5 _ of LiF and 2500 _ of aluminum on the electron-transporting layer so as to prepare a organic light-emitting device. In the process, the deposing

speed was maintained by 1 to 3 _/sec for depositing NPB and Alq3, 0.2 to 0.3 _/sec for lithium fluoride, and 3 to 7 _/sec for aluminum. The total thickness of layers of the organic light-emitting device was 1750_.

FIG. 3 illustrates voltage-brightness relationship for the manufactured organic light-emitting device. Measuring a life of the device was carried out in the constant current (DC) density of 60 mA/cm^2, and the decrease of relative brightness with operating time was illustrate in FIG. 4.

(Example 2)

An organic light-emitting device was manufactured by using the same process of Example 1, except that a compound represented by Chemical Formula 2 was used in the hole-injecting layer having a thickness of 1500 _. The total thickness of organic layers consisting the organic light-emitting device was 2500_. A voltage-brightness relationship and a life of the device were measured by same method of Example 1 and the results were illustrate in FIGs. 3 and 4.

(Comparative Example 1)

An organic light-emitting device was manufactured using by the same process of Example 1, wherein hole-injecting layer was formed by deposing copper phthalocyanine complex having thickness of 150 _ instead of Chemical Formula 2. The total thickness of organic layers consisting the organic light-emitting device was 1150_. A voltage-brightness relationship and a life of the device were measured by same method of Example 1 and the results were illustrated in FIGs. 3 and 4.

As shown in the Examples and Comparative Example, the organic light-emitting device comprising the compound represented by Chemical Formula 2 that is one of examples satisfying Chemical Formula 1 as a hole-injecting material was operated by low drive-voltage and showed improved life than the organic light-emitting device comprising common copper phthalocyanine complex. Furthermore, the organic light-emitting device of Example 2, which was prepared by using the compound represented by Chemical Formula 2 that is one of examples satisfying Chemical Formula 1 to the hole-injecting layer having a thickness of 1500_, shows very small elevation of operating drive-voltage. The above result presents that the compound represented

by Chemical Formula 1 has superior hole-injecting ability and superior hole-transporting ability, and can be formed stable interface with the electrodes.

【 RESULT OF THE INVENTION】

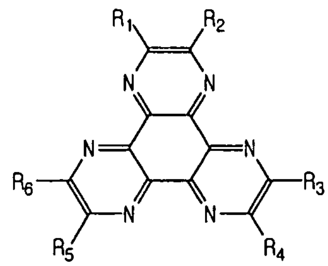
The organic light-emitting device comprising the compound of the Chemical Formula 1 having characteristics of p-type semiconductor can be operated by low drive-voltage and shows improved life. Therefore, the device may be an organic thin film transistor, a photovoltaic cell, an OPC of laser printer or a cloying press, etc.

【 WHAT IS CLAIMED】

【 Claim 1】

An organic light-emitting device comprising a compound represented by Chemical Formula 1 in at least one of hole-injecting layer and hole-transporting layer:

[Chemical Formula 1]



wherein, R_1 to R_6 is independently or simultaneously selected from the group consisting of hydrogen atom, C_1-C_{12} hydrocarbon, halogen, alkoxy, arylamine, ester, amide, imide, aromatic hydrocarbon, heterocyclic compound, nitro, and nitrile (-CN) group).

【 Claim 2】

The organic light-emitting device according to Claim 1, wherein R_1 to R_6 are simultaneously ester, amide, nitro, or nitrile group.

【 Claim 3】

The organic light-emitting device according to Claim 1, wherein the device comprises in order:

a) a transparent substrate;

b) an anode;

c) a hole-injecting layer;

d) a light-emitting and electron-transporting layer; and

e) a cathode.

【 Claim 4】

The organic light-emitting device according to Claims 1 or 3, wherein the anode comprises a conducting polymer, or a conducting metal oxide.

【 Claim 5】

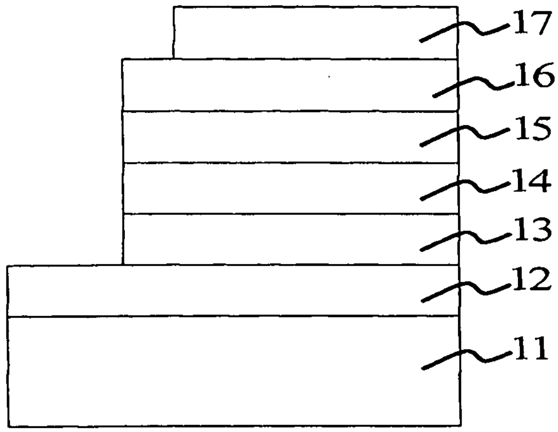
The organic light-emitting device according to Claim 3, wherein a hole-transporting layer is further comprised between b) anode and c) hole-injecting layer.

【 Claim 6】

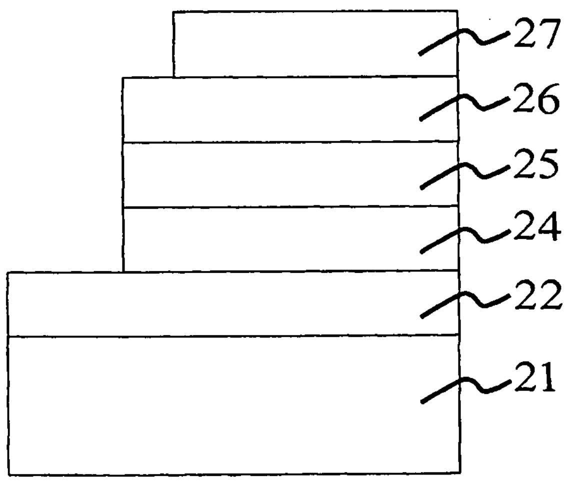
The organic light-emitting device according to Claim 5, wherein the thickness of the hole-injecting layer and hole-transporting layer is 0.1 to 10,000 nm, respectively.

【 FIGURES】

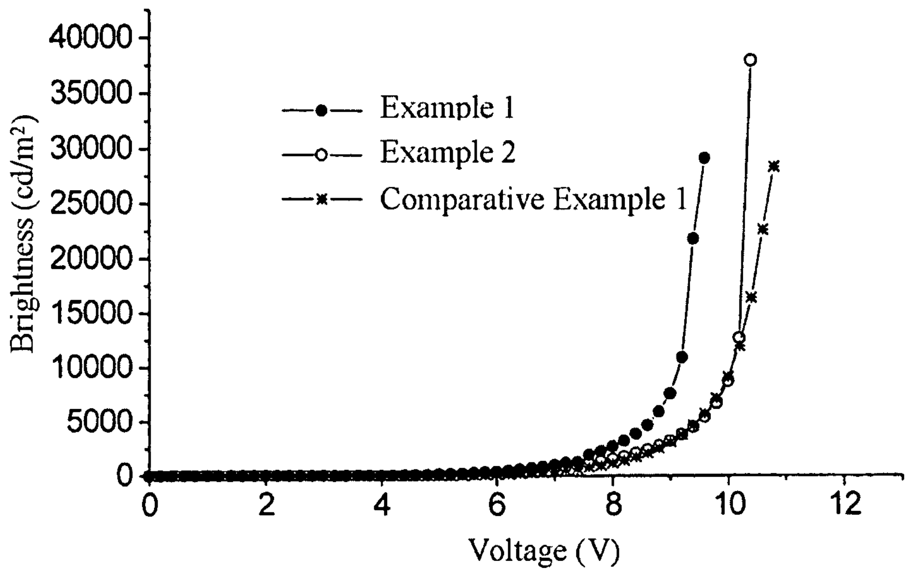
【 FIG. 1】



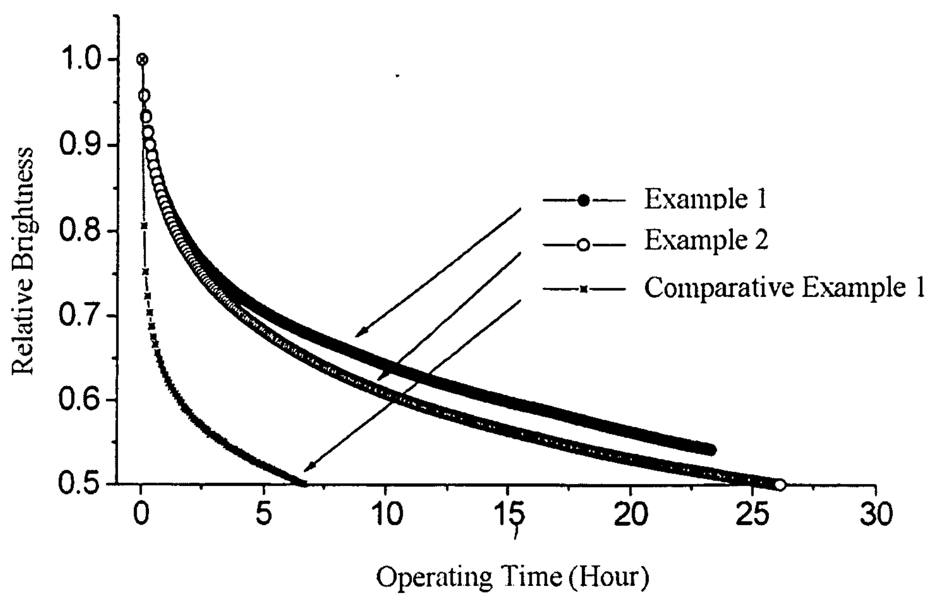
【 FIG. 2】



【 FIG. 3】


40000
35000
30000
25000
20000
15000
10000
5000
0
Brightness (cd/m²)
Example 1
Example 2
Comparative Example 1
0
2
4
6
8
10
12
Voltage (V)

【 FIG. 4】


1.0
0.9
0.8
0.7
0.6
0.5
Relative Brightness
Example 1
Example 2
Comparative Example 1
0
5
10
15
20
25
30
Operating Time (Hour)